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PATENT SPECIFICATION

NO DRAWINGS

1,173,027



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Date of filing Complete Specification: 29 May, 1968.

Date of Application (No. 36076/67): 7 Aug., 1967.

Complete Specification Published: 3 Dec., 1969.

Index at acceptance:—A5 E(1C1B, 1C4A2, 1C4A3, 1C4B2, 2)

International Classification:—A 01 n 17/10

COMPLETE SPECIFICATION

Improvements in Mothproofing

We, SHELL INTERNATIONALE RESEARCH MAATSCHIPPIJ N.V., a company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in mothproofing techniques, and in particular to a technique whereby an insecticide can be applied to a fabric from an aqueous bath containing the insecticide dispersed in a solid particulate form.

Industrial mothproofing has, in the past, largely been dominated by the use of Dieldrin applied to wool from an aqueous medium, and in almost all subsequent work on the development of new mothproofing agents, and in examining the affinity of insecticides to wool, the insecticide has been applied to the wool either from an aqueous emulsion or from a solution in an organic solvent. The application of particulate insecticides through the use of pastes or powder formulations has hitherto been neglected, despite the fact that such formulations would be cheaper than emulsions, and would avoid the use in the treatment bath of solvents, such as xylene, whose vapours can cause toxic hazards during the treatment. It has now surprisingly been found that those insecticides which have a water solubility below 100 ppm at 20°C may be applied to fabrics from an aqueous particulate dispersion in a manner analogous to that employed in disperse dyeing.

Accordingly, the present invention provides a process for mothproofing fabrics, in which the fabric is immersed in a proofing medium containing an insecticide in a disperse solid form, wherein the proofing medium is formed by dispersing in water a formulation comprising an insecticide of water solubility below 100 ppm at 20°C in the form of solid par-

ticles having a mass median diameter not greater than 4 μ . The water solubility of the insecticide should preferably be below 10 ppm at 20°C. Preferably the formulation is a solid formulation, especially one in which the insecticide is absorbed onto a solid filler, such as a wettable powder containing the insecticide, a solid filler, and a surfactant. Preferred solid fillers include synthetic silicas, synthetic aluminosilicates, kaolinates, attapulgites, diatomaceous earths and talcs. Other suitable formulations include flowable pastes containing the insecticide, at least one surfactant, a suspending liquid, suitably water, and optionally also a stabilising agent. Whatever the nature of the formulation used, there should preferably be no, or at most 15% by weight of, particles whose size is greater than 5 μ .

When a wettable powder formulation is used it may conveniently contain 50—90% by weight of insecticide, 3—15% by weight of at least one surfactant (preferably anionic) and the remainder being an inert solid filler.

When a flowable paste formulation is used it conveniently contains 20—60% by weight insecticide, 1—25% by weight of one or more nonionic or anionic surfactants, and may contain 0.1—10% w of protective colloids or thixotropic agents to stabilise the suspension, the remainder of the material usually being water or an aqueous solution of an inorganic salt. Examples of suitable protective colloids are polyvinyl alcohols, cellulose derivatives such as hydroxyethyl cellulose, natural gums and colloids, and carboxylated polyelectrolytes. Examples of thixotropic agents are bentonites, and natural and synthetic silicas, silicates, and aluminosilicates. When an inorganic salt is used, it may be added to the water in a flowable paste to stabilise the suspension by matching the density of the aqueous phase to that of the insecticide particles; examples of suitable salts are the highly soluble ammonium, sodium,

potassium, magnesium or calcium salts of hydrochloric, sulphuric or nitric acid.

- The term "solid filler" as used herein means a material, which may be inorganic and of synthetic or natural origin, with which the active compound is mixed or formulated to facilitate its application to the fabric or its storage, transport or handling. Examples of suitable solid carriers are natural silicas such as diatomaceous earths; magnesium silicates for example, talcs; magnesium aluminium silicates, for example, attapulgites and vermiculites; aluminium silicates, for example, kaolinites, montmorillonites and micas; calcium carbonates; synthetic hydrated silicon oxides and synthetic calcium or aluminium silicates.

The surface-active agent may be a wetting agent, an emulsifying agent or a dispersing agent; it may be nonionic or ionic. Any of the surface-active agents usually applied in formulating insecticides may be used. Examples of suitable surface-active agents are the sodium or calcium salts of polyacrylic acids and lignin sulphonic acids, the condensation products of fatty acids or aliphatic amines or amides containing at least 12 carbon atoms in the molecule with ethylene oxide and/or propylene oxide; fatty acid esters of glycerol, sorbitan, sucrose or pentaerythritol and condensates of these with ethylene oxide and/or propylene oxide; condensation products of fatty alcohols or alkyl phenols, for example *p*-octylphenyl or *p*-octylcresol, with ethylene oxide and/or propylene oxide; sulphates or sulphonates of these condensation products; alkali or alkali metal earth metal salts of sulphuric or sulphonic acid esters containing at least 10 carbon atoms in the molecule, for example, sodium lauryl sulphate, sodium secondary alkyl sulphates, sodium salts of sulphonated castor oil, and sodium alkylaryl sulphonates such as sodium dodecylbenzene sulphonate; polymers of ethylene oxide and copolymers of ethylene oxide and propylene oxide.

The present invention was developed as a consequence of work intended to establish whether an insecticide of low water solubility could be applied to a fabric for mothproofing purposes by a mechanism similar to that by which a disperse dye is applied to a fabric. Disperse dyes are crystalline compounds which are soluble in organic solvents, and have a low, but definite, solubility in water. Because of their low aqueous solubility, these dyes are applied to fibres from a very fine aqueous dispersion in the dye-bath. The dye passes into the fibre by the following mechanism. The solid particles in the aqueous dispersion dissolve in the water to an extent sufficient to provide saturation of the aqueous phase, and the dye then partitions between the fibre and the saturated aqueous phase, whilst the saturation of the aqueous phase is maintained by continuous dissolution of the

solid dye particles as the dye is absorbed by the fibre. Since the dye normally has a relatively high solubility in the fibre as compared with the water, nearly all the dye is eventually absorbed by the fibre leaving only a very small quantity in the bath liquor. As indicated above, it has now been discovered, and forms the subject of the present invention, that insecticides of low water solubility can be applied to fabrics, such as wool, by a mothproofing technique analogous to the disperse dyeing process. It will, of course, be appreciated that the close analogy between the disperse mothproofing technique of the present invention and the known technique of disperse dyeing, means that many of the specialized techniques developed for disperse dyeing (for example, the use of dye carriers and mixtures of dyes) can be applied (with appropriate modification where necessary) to facilitate and enhance the effectiveness of disperse mothproofing.

In addition to the absorption of the insecticide into the fibre via the saturated aqueous phase as described above, some attraction of the insecticide-containing solid particles to the surface of the fibres also occurs (as in the case with disperse dyeing). However, the binding of the insecticide to the fibre is of a quite different nature in the two cases; in the former case the insecticide is strongly absorbed in the fibre and is fast to washing and dry cleaning, whilst in the latter case crystals of insecticide are loosely held on the fibre surface and are readily removed by washing and agitation in dry cleaning solvents, such as white spirit and perchloroethylene.

For certain mothproofing applications where fastness to washing, dry cleaning, pressing, rubbing, sea-water, sunlight, etc., is not required, the presence of surface crystalline material may be acceptable. In this case, the amount of insecticide added to the bath will depend on the degree of proofing required, with application rates preferably between 0.01% w and 2.0% w active material based on the weight of the fabric. Only a small surfactant concentration suitable to provide an initial dispersion of the insecticide is required, preferably between 0.1 mg and 100 mg per litre of bath liquor, which may be added as a constituent of the formulation.

However, where long-term proofing of a woollen article is required, good fastness properties are essential, and it is clearly desirable for the mothproofing conditions to be so selected that most, if not all, of the insecticide is absorbed into the fibre, thereby achieving the maximum proofing effect. Insecticides have been found to exhibit a maximum absorption or saturation value in wool when applied from an aqueous bath in a similar manner to disperse dyes. For most nonionic insecticides, this value appears to

lie in the range 0.01% w to 0.5% w on the weight of the wool (the actual value varying not only with the insecticide used, but also varying with different batches of wool) and the preferred application rate of the insecticide therefore lies within these condensation limits since addition insecticide applied beyond the saturation value can only form a surface deposit, whereas only the absorbed material is likely to be effective for long-term mothproofing.

For certain proofing requirements it may be necessary to increase the rate at which the insecticide is absorbed into the fabric. As indicated above, a surfactant concentration of 0.1—100 mg per litre of bath liquor is normally suitable to provide an adequate dispersion of insecticide; however, it has been found that the use of larger quantities of surfactant e.g. 100 mg—5,000 mg per litre of bath liquor, often produces a more rapid rate of insecticide absorption into the fabric and frequently also reduces the deposition of crystalline insecticide on the surface of the fabric fibres. Ionic surfactants are, in general, the most effective at increasing the rate of insecticide absorption, whilst nonionic surfactants are generally the most effective at reducing the deposition of crystalline insecticide.

Under some circumstances it may also be desirable to increase the amount of insecticide absorbed beyond the saturation value. It has been found that the presence of certain organic solvents in the bath liquor alters the absorption equilibrium, and so frequently enables an insecticide absorption value in excess of the saturation value to be achieved. Suitable organic solvents includes alcohols and esters, cyclohexanol having been found of particular value in increasing the absorption of β -dihydroheptachlor into wool.

When it is not found practicable to achieve the desired level of mothproofing by the procedures so far described, it is often possible to increase the degree of mothproofing by the use of a combination of more than one insecticide. If one insecticide is present in the bath liquor in conditions and amounts sufficient to give the maximum possible absorption into the fibre, then clearly the mothproofing effectiveness of that insecticide is at its optimum. However, the fact that the fibre is saturated with respect to one insecticide does not mean that it is saturated with respect to all insecticides, and it is therefore often possible to incorporate a second insecticide into a fibre already saturated with respect to a first insecticide. The additional insecticide(s) may be added to the bath liquor as a separate formulation, or may be incorporated with the original insecticide in a single formulation.

The process of the present invention may

be applied to proof any moth-susceptible fabric against any moth, beetle or other keratin-digesting insect by the choice of an insecticide active against the particular insect concerned. Suitable types of insecticide include chlorinated hydrocarbons, vinyl phosphates and carbamates.

The invention is illustrated in the following Examples.

EXAMPLE I.

The mothproofing effectiveness of various formulations was determined by measuring the uptake of insecticide into the wool and its fastness properties in wool. Two types of wool material were used; i) 'Avebury flannel', which is the standard flannel as used in the Avebury mothproofing test. It is known to the textile trade as 'doctor' flannel (Kellsall and Kemp Ltd., Rochdale) and is an all wool, unbleached white flannel, 64s quality Merino wool, with a fibre diameter of 20—25 μ , and a weight of ca. 185 g/m²; and ii) 2/55s Greatwich Carpet Yarn, scoured and undyed.

The following insecticide formulations were used:

- β - Dihydroheptachlor (2 - exo - 4,5,6,7,8,8-heptachloro - 3a, 4, 7,7a - tetra - hydro-4,7 - methanoindane). 90
 (a) 50% w/w flowable paste. This formulation contained 50% w toxicant and the remainder a non-ionic surfactant solution (Nekanil* O solution). 95
 (b) 75% w wettable powder. This formulation contained 5% w of anionic surfactants (Tamoi 731+Empicol* LZ) and the remainder an inert filler (synthetic silica). 100
 (c) 8% w/w emulsifiable concentrate. This formulation contained 10% w of a non-ionic surfactant (Nonidet* P40), and the remainder xylene. It contained the maximum concentration of β -dihydroheptachlor which can be dissolved in a formulation similar to "Dielmoth" without showing crystallisation at 0°C.

*registered Trade Mark.

The particulate formulations (a) and (b) were seen under the microscope to contain particles of average size 1—2 μ with very few particles above 5 μ . Formulation (c) was included for comparative purposes.

Dieldrin [Commercial dieldrin as defined contains a minimum of 85% w of HEOD (1,2,3,4,10,10 - hexachloro - 6,7 - epoxy-1,4,4a,5,6,7,8,8a - octahydro - 1,4 - endo,exo-5,8 - dimethanonaphthalene)].

This was used as 'Dielmoth' a 20% w/w emulsifiable concentrate based on xylene as supplied commercially by Shell Chemical Co. Ltd.

The insecticide formulations were applied at the boil to the Avebury flannel and carpet yarn under the following conditions:—

Application rate (based on the wool weight)	: β -dihydroheptachlor 0.20% w nominal dieldrin 0.05% w nominal
Water	: Zeolite softened water of zero hardness.
Wool	: 9" x 96" piece of Avebury flannel (weight approximately 100 g). Eight hanks of Greatwich carpet yarn (each weighing approximately 10 g).
Wool pre-treatment	: Wet out in boiling water for 3 minutes and rinsed in cold water.
Bath	: For Avebury flannel, a laboratory model stainless steel winch bath heated with live steam. For Greatwich yarn, a glass beaker heated on a hot plate (no live steam) with yarn hanks suspended from a v-shaped glass rod. The rod was agitated at frequent intervals during the treatment.
Liquor	: pH 4 (acetic acid added).
Liquor to wool ratio	: 20 : 1
Formulation	: An accurately weighed quantity was uniformly dispersed in approximately 30 ml of water and then added with stirring to the cold bath.
Heating	: 30 minutes from room temperature to the required temperature. Maintained at the required temperature for 30 minutes (Avebury flannel) or 1 hour (Greatwich yarn).
Rinsing	: A first rinse in about 2-2½ litres cold water, and a second rinse in about 8 litres of cold water. Finally passed through a wringer.
Drying	: Wool divided into two parts and line dried for 24 hours at room temperature for uptake data, and for 1½ hours at 50°C for wash fastness tests.

- 5 The wash fastness of the insecticide was measured using 10 g hanks (Greatwich yarn) of 17 g pieces (Avebury flannel) which were given a hand wash test in a solution containing 2 g/litre "Lux"® soap flakes and 2 g/litre anhydrous Na₂CO₃, with a liquor to wool ratio of 20:1. (*registered Trade Mark). The temperature of the solution was 45°C and the time of immersion 5 minutes. Agitation and squeezing by hand was carried out
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intermittently for about 50% of the time of the immersion. The fabric was rinsed at 45°C for 30 seconds at a liquor to wool ratio of 20:1, dried for 1½ hours at 50°C and then analysed. 15

The wool samples were systematically subsampled into 1 inch squares of 12" strands, sufficient being taken to provide approximately 1.5 g of wool per analysis; duplicate determinations were made. The amount of in- 20

secticide taken up by the wool, the amount remaining after the wash fastness test just described, and the amount remaining after giving the wool four 15 minute rinses in white spirit at 32°C to remove the surface deposit of insecticide, was determined by extracting appropriate wool samples in a Soxhlet apparatus with azeotropic solvent of 39% volume methanol, 61% volume benzene. Aliquots of the extract were appropriately diluted with petroleum spirit to give a concentration suit-

able for gas liquid chromatographic (GLC) analysis using electron capture detection.

The wool samples obtained in the wash fastness tests were bioassayed at the Huntingdon Research Centre according to the Avebury Mothproofing Test, and all were satisfactorily proofed against 3 week old *Tineola bisselliella* larvae.

The results of these experiments are given 20 in Table 1.

TABLE I
The Comparison of the performance of β -dihydroheptachlor formulations and 'Dielmoth'

Details	Application*				Wash fastness**						State in wool*		
	% w nominal	mg added to bath ⁺	mg found in wool	% uptake	No. of washes—% w in wool						Total % w in wool	% w absorbed in wool	Absorbed insecticide as % of total
					0	1	3	5	10				
A. Avebury Flannel													
1. β -dihydroheptachlor													
(a) 50% w/w paste-													
(initial	0.20	217.2	131.3	60.5	0.131	0.105	0.091	0.089	0.064	0.134	0.113	0.113	84
(duplicate	0.20	208.6	129.1	61.9	0.126	0.113	0.094	0.082	0.070	0.132	0.119	0.119	90
(b) 75% w wettable powder	0.20	219.4	119.7	54.6	0.108	—	—	—	0.067	0.116	0.103	0.103	89
(c) 8% w/w emulsifiable concentrate	0.20	215.3	114.6	53.2	0.123	0.091	0.082	0.068	0.057	0.113	0.093	0.093	82
2. Dieldrin													
(Dielmoth) (initial	0.05	52.1	37.2	71.4	0.038	0.031	0.024	0.022	0.015	0.037	0.036	0.036	97
(duplicate	0.05	49.4	33.9	68.6	0.037	0.031	0.024	0.024	0.015	0.037	0.037	0.037	100

TABLE I—Continued

The Comparison of the performance of β -dihydroheptachlor formulations and 'Dielmoth'

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Details	Application*			Wash fastness**						State in wool*		Absorbed insecticide as % of total	
	% w nomin-al	mg added to bath ⁺	mg found in wool	% uptake	No. of washes—% w in wool						Total % w in wool	% w absorbed in wool	
					0	1	3	5	10				
B. Greatwich Carpet Yarn													
1. β -dihydroheptachlor													
(a) 50% w paste	(initial)	0.10	89.5	60.5	67.7	0.077	0.066	—	0.058	—	0.074	0.068	92
	(duplicate)	0.10	90.0	67.0	74.5	0.079	0.068	—	0.059	—	0.081	0.073	90
(b) 75% w wettable powder		0.10	84.5	57.4	67.9	0.069	—	—	0.056	—	0.072	0.063	88
2. Dieldrin													
'Dielmoth' (initial)		0.03	26.0	24.1	92.7	0.029	0.024	—	0.020	—	0.028	0.025	89
	(duplicate)	0.03	26.7	21.0	78.6	0.027	0.021	—	0.019	—	0.025	0.024	96

*Wool dried 24 hours at room temperature; **Wool dried 1½ hours at 50°C; ⁺Calculated using the β -dihydroheptachlor or dieldrin content as determined by analysis.

EXAMPLE II.

- The mothproofing effectiveness of β -dihydroheptachlor, Dieldrin, DDT, Gardona* [2 - chloro - 1 - (2,4,5 - trichlorophenyl) vinyl phosphate] and Land-rin* [3,4,5-trimethylphenyl N-methyl carbamate] when formulated as wettable powders was examined in further experiments. The insecticides were formulated in the following manner:
- 5 (a) 50% w β -dihydroheptachlor wettable powder. This formulation contained 5% w of anionic surfactants (Tanol 731 and Empicol LZ) and the remainder a kaolinite (Speswhite*).
 - 10 (b) 50% w dieldrin wettable powder. This formulation contained 10% w of anionic surfactants (Tanol 731 and Empicol LZ) and the remainder an attapulgite (Florisil*).
 - 15 (c) 50% w DDT wettable powder. This formulation contained 10% w of anionic surfactants (Tanol 731 and Empicol LZ) and the remainder a synthetic aluminosilicate (Alusil*).
 - 20 (d) 50% w Gardona wettable powder. This formulation contained 10% w of anionic surfactants (Tanol 731 and Empicol LZ) and the remainder a diatomaceous earth (Microcel 8E).
 - 25 (e) 50% w Landrin wettable powder. This formulation contained 12% w of anionic surfactants (Tanol 731, Empicol LZ and Aerosol OT/B) and the remainder a talc (Talc S2N).

*registered Trade Mark.

The first four wettable powders were seen under the microscope to contain particles of average size 1—2 μ with few particles above 5 μ . The Landrin wettable powder had an average particle size of 1—5 μ with few particles above 10 μ ; since this insecticide has

the greatest water solubility (89 ppm at 22°C) this larger particle size was considered acceptable.

These formulations were applied to Avebury Flannel and the treated wool washed in soap and soda and rinsed in white spirit according to the procedures described in Example I, except that the application temperature was 90°C and the wool samples were dried for 24 hours at room temperature only.

Wool samples give 0 washes, 10 washes, and 4 white spirit rinses (i.e. containing absorbed insecticide only) were bioassayed at the Huntingdon Research Centre according to the Avebury Mothproofing Test. All samples, except the 10 wash samples of Gardona and Landrin, were proofed against 3 week old *Tineola bisselliella* larvae.

The wool samples treated with β -dihydroheptachlor, dieldrin, DDT and Landrin were extracted and analysed as described in Example I. With the Landrin treated wool given 10 washes, background interference on the GLC trace prevented an accurate determination of the Landrin content; it was indicated that the Landrin content was very small. The wool samples treated with Gardona showed incomplete extraction of the insecticide with the benzene/methanol solvent, and no alternative extraction solvent has been found. The wool samples were therefore analysed for chlorine content by oxygen flask combustion, absorption into hydrazine sulphate solution and potentiometric titration with silver nitrate solution. The results are expressed as Gardona content, but as the Gardona may have partially hydrolysed in the bath, the results may have a contribution due to Gardona decomposition products. All the results are given in Table 2.

TABLE 2
The performance of insecticide wettable powders

Wettable powder	Application				Wash fastness			State in wool	
	% w nominal	mg added to bath*	mg found in wool	% uptake	No of washes—% w in wool	0	10	Total % w in wool	% w absorbed in wool
1. β -dihydroheptachlor/kaolinite	0.20	215.5	145.1	67.2	0.141	0.075	0.141	0.125	89
2. Dieldrin/attapulgite	0.05	57.2	48.5	84.8	0.047	0.021	0.047	0.047	100
3. DDT/synthetic aluminosilicate	0.20	210	210	100	0.21	0.12	0.21	0.19	90
4. Gardona/diatomaceous earth	1.0	1066	612	57	0.60	0.11	0.60	0.60	100
5. Landrin/talc	1.0	1051	106	10	0.10	interference**	0.10	0.095	95

* Calculated using the insecticide content of the formulation as determined by analysis.

** Background interference on the GLC trace prevented an accurate determination.

EXAMPLE III.

Applications of β -dihydroheptachlor to Avebury Flannel at various dosage rates up to 0.25% w nominal, using a winch bath and raising the temperature to 40°C over half-an-hour and maintaining 40°C for a further half-an-hour, have shown that in these conditions the β -dihydroheptachlor absorbed by the wool is about 0.01% w, too low for satisfactory proofing of the wool. The maximum absorption of β -dihydroheptachlor in wool observed for an aqueous bath at 40°C was 0.026% w after 48 hours treatment at 0.40% w nominal β -dihydroheptachlor; this value is presumed to be close to the absolute maximum or saturation value of β -dihydroheptachlor when applied from water at 40°C. Experiments were therefore carried out on the effect of carriers in the bath liquor to increase the absorption of β -dihydroheptachlor by wool at 40°C. An 85% w wettable powder, containing 7.5% anionic surfactants (Tanol 731, Empicol LZ and Aerosol OT/B) and the remainder of synthetic silica (Silicium dioxide No. 3) and of average particle size 1–2 μ , with few particles above 5 μ , was

prepared. Using the procedures described in Example I except that a neutral bath was used, 0.20% w nominal β -dihydroheptachlor was applied to Avebury Flannel in the presence of various carriers, the treated wool rinsed in white spirit to determine the absorbed insecticide, and the wool samples analysed. Many additives had little or no effect on the absorption of β -dihydroheptachlor, but certain solvents and surfactants did increase the absorption, as given in Table 3.

From the results it can be seen that certain surfactants e.g. Empicol LZ Nonidet P 40, Sorbester^{*} Q 17, have reduced the deposition of crystalline β -dihydroheptachlor on the wool surface, whilst all the surfactants increased the rate of absorption of insecticide into the wool. (*registered Trade Mark). Certain of the solvents, in particular, cyclohexanol, n-hexanol, and ethyl acetate, increased the absorption above that found in the 48 hour treatment.

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TABLE 3

Effect of carriers on the uptake of β -dihydroheptachlor by wool at 40°C. using 1 hour treatments

Type	Carrier	Carrier Concentration in bath liquor % w/v	Total	Absorbed
1. None (1 hour treatment)	—	—	0.041	0.007
None (48 , ,)	—	—	0.175	0.026
2. Anionic surfactants	Tensiofix KL	0.2	0.053	0.022
	Empicol LZ	0.2	0.020	0.020
	Manoxol [*] OT	0.2	0.026	0.018
3. Nonionic surfactants	Nonidet P 40	0.2	0.013	0.012
	Sorbester Q 17	0.2	0.015	0.014
4. Cationic surfactant	Cetyl trimethyl ammonium bromide	0.2	0.027	0.022
5. Solvents	Cyclohexanol	4.8	0.124	0.073
	N-Hexanol	0.8	0.098	0.039
	Ethyl acetate	6.5	0.070	0.039
	Methyl isobutyl carbinol	1.5	0.132	0.032
	n-Butanol	6.6	0.060	0.024
	Benzyl alcohol	4.1	0.056	0.017
6. Phenols	Thymol	1.0	0.135	0.025
	Salicylic acid	0.5	0.137	0.018

* registered Trade Mark

EXAMPLE IV.

Experiments on applying different application rates of β -dihydroheptachlor to wool have shown that the optimum application rate at the boil is 0.20% w nominal β -dihydroheptachlor. At higher application rates, large increases in the β -dihydroheptachlor added to the bath bring about only slight increases in the β -dihydroheptachlor absorbed by the wool, and consequently only slight improvements in the proofing effect are obtained. At an application rate of 0.20% w nominal β -dihydroheptachlor, the proofing against 6 month old *Attagenus piceus* larvae is in the borderline region at 3 washes. To improve this performance an experiment was carried out applying to wool a mixture of β -dihydroheptachlor and chlordene, which are equally active against *A. piceus*.

A wettable powder containing 16.8% w β -dihydroheptachlor, 32.1% w chlordene, 5% w of anionic surfactants (Tamol 731 and Empicol LZ) and a kaolinite (Clay GTY) was finely milled, after which it was seen under the microscope to contain particles of average size 1—2 μ , with few particles above 5 μ . Using this wettable powder, duplicate applications of 0.15% w nominal β -dihydroheptachlor, 0.30% w nominal chlordene were

made to Avebury Flannel at the boil. The treated wool samples were washed in soap and soda and rinsed in white spirit. Chemical analyses of the wool samples are given in Table 4. Along with wool samples from the 50% w β -dihydroheptachlor paste applications described in Example I, the wool samples were bioassayed at the Huntingdon Research Centre against 3 week old *T. Bisselliella* and 6 month old *A. Piceus* larvae. All the samples were proofed against *T. bisselliella*; the *A. piceus* results are given in Table 5.

The same experimental conditions as given in Example I were used throughout this Example, with the exception that a different batch of Avebury Flannel was used. It has been found that this particular batch of flannel will absorb only two-thirds the quantity of β -dihydroheptachlor absorbed by the flannel used in Example I; application of 0.20% w nominal β -dihydroheptachlor gives a maximum of 0.08% w β -dihydroheptachlor in wool (Table 3). This example therefore shows that the application of two insecticides has not only overcome the poorer absorption characteristics of the flannel used, but has also given a better proofing of the flannel against *Attagenus piceus* than given by β -dihydroheptachlor alone.

TABLE 4
Performance of a β -dihydroheptachlor/chlordene wettable powder

Details	Application**			Wash fastness***					State in wool**		
	% w-nomin-al	mg added to bath*	mg found in wool	% uptake	No. of washes—% w in wool					Total % w in wool	Absorbed insecticide as % of total
					0	1	3	5	10		
1. Initial application	% w-nomin-al	mg added to bath*	mg found in wool	% uptake	0	1	3	5	10	Total % w in wool	Absorbed insecticide as % of total
	0.15	150.9	78.8	52.2	0.062	0.042	0.036	0.033	0.027		
Chlordene	0.30	288.3	89.9	31.2	0.081	0.062	0.055	0.051	0.041	0.089	0.079
2. Duplicate application	% w-nomin-al	mg added to bath*	mg found in wool	% uptake	0	1	3	5	10	Total % w in wool	Absorbed insecticide as % of total
	0.15	144.8	85.4	59.0	0.066	0.046	0.039	0.038	0.032		
Chlordene	0.30	276.7	99.9	36.1	0.089	0.064	0.059	0.057	0.049	0.103	0.090
3. β -dihydroheptachlor alone	0.20	197.8	122.8	62.1	0.117	—	—	0.053	—	0.124	0.074

* Calculated using the insecticide of the formulation as determined by analysis.

** Wool dried 24 hours at room temperature

*** Wool dried 1½ hours at 50°C.

TABLE 5
Bioassay against Attegenus piceus

Number of soap/soda washes	β -dihydroheptachlor alone		β -dihydroheptachlor/chlordan	
	Initial	Duplicate	Initial	Duplicate
0	P	P	P	P
1	P	P	P	P
3	P	BP	P	P
5	NP	NP	P	P
10	NP	NP	BP	P

P = Proofed

BP = Borderline proofed

NP = Not proofed

WHAT WE CLAIM IS:—

1. Process for mothproofing fabrics, in which the fabric is immersed in a proofing medium containing an insecticide in a disperse solid form, wherein the proofing medium is formed by dispersing in water a formulation comprising an insecticide of water solubility below 100 ppm at 20°C in the form of solid particles having a mass median diameter not greater than 4 μ . 45
2. Process according to claim 1 wherein the water solubility of the insecticide is below 10 ppm at 20°C. 50
3. Process according to claim 1 or 2 wherein in the formulation is a solid formulation in which the insecticide is absorbed onto a solid filler. 55
4. Process according to claim 3 wherein the formulation is a wettable powder containing the insecticide, a solid filler, and at least one surfactant. 60
5. Process according to claim 4 wherein the solid filler is a synthetic silica, a synthetic aluminosilicate, a kaolinite, an attapulgite, a diatomaceous earth, or a talc. 65
6. Process according to claim 4 or 5 wherein in the wettable powder contains 50—90% by weight insecticide, 3—15% by weight surfactant(s) and solid filler to make 100%. 70
7. Process according to claim 1 or 2 wherein in the formulation is a flowable paste containing the insecticide, at least one surfactant, a suspending liquid, and optionally also a stabilising agent. 75
8. Process according to claim 7 wherein the suspending liquid is water, or an aqueous solution of an inorganic salt. 80
9. Process according to claim 8 wherein the flowable paste contains 20—60% by weight insecticide, 1—25% by weight of one or more nonionic or anionic surfactants, 0.1—
- 10% by weight of a protective colloid or a thixotropic agent, and water or an aqueous solution of an inorganic salt, to make 100%. 45
10. Process according to any one of the preceding claims wherein the formulation contains at most 15%, by weight of particles whose size is greater than 5 μ . 50
11. Process according to any one of the preceding claims wherein the formulation is dispersed in the water in an amount sufficient to provide an amount of insecticide between 0.01% and 2.0% by weight based on the weight of the fabric to be mothproofed. 55
12. Process according to claim 11 wherein the formulation is dispersed in the water in an amount sufficient to provide an amount of insecticide between 0.01% and 0.5% by weight based on the weight of the fabric to be mothproofed. 60
13. Process according to any one of the preceding claims wherein the formulation is dispersed in the water in an amount sufficient to provide an amount of surfactant between 0.1 mg and 100 mg per liter of proofing medium. 65
14. Process according to any one of claims 1—12 wherein the formulation is dispersed in the water in an amount sufficient to provide an amount of surfactant between 100 mg and 5,000 mg per litre of proofing medium. 70
15. Process according to any one of the preceding claims wherein an organic solvent is additionally incorporated into the proofing medium. 75
16. Process according to claim 15 wherein the organic solvent is an alcohol or an ester. 80
17. Process according to any one of the preceding claims wherein at least two different insecticides of water solubility below 100 ppm at 20°C are dispersed in water to form the proofing medium.

18. Process according to any one of the preceding claims wherein the insecticide is a chlorinated hydrocarbon, a vinyl phosphate or a carbamate.
- 5 19. Process for mothproofing fabrics according to claim 1 by immersion in an aqueous dispersion of insecticide substantially as hereinbefore described.
20. Fabrics when mothproofed by a process according to any one of the claims 1—19.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
copies may be obtained.